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Article

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In-situ mapping of the molecular arrangement of amphiphilic dye molecules at the TiO₂ surface of dye sensitized solar cells

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simulations, liquid phase

ABSTRACT

Amphiphilic sensitizers are central to the function of dye-sensitized solar cells. It is known that the cell's performance depends on the molecular arrangement and the density of the dye on the semiconductor surface, but a molecular-level picture of the cell-electrolyte interface is still lacking. Here, we present sub-nanometer *in-situ* atomic force microscopy images of the Z907 dye at the surface of TiO₂ in a relevant liquid. Our results reveal changes in the conformation and the lateral arrangement of the dye molecules, depending on their average packing density on the surface. Complementary quantitative measurements on the ensemble of the film are obtained by a quartz-crystal microbalance with dissipation technique. An atomistic picture of the dye coverage-dependent packing, the effectiveness of the hydrophobic alkyl chains as blocking layer and the solvent accessibility is obtained from molecular dynamics simulations.

1. Introduction

Surface functionalization with self-assembled monolayers (SAMs) is of fundamental importance to nanotechnology, with applications ranging from molecular electronics to controlled wetting, sensing, medical devices and energy harvesting systems.¹⁻⁵ SAM functionalization provides a powerful, yet simple way to manipulate the chemical, electrical and optical properties of surfaces, with the ability to tune the material's macroscopic properties.⁶ This is the case for dye-sensitized solar cells (DSCs) where a SAM of dye molecules sensitizes a semiconductor in order to harvest light. DSCs provide a viable alternative to traditional semiconductor solar cells due to their high efficiency and low environmental and industrial

costs.^{5,7-11} The heart of the DSC is composed of the dye SAM adsorbed on a wide-bandgap semiconductor, usually a high surface area mesoporous TiO₂ photoanode, infiltrated with an electrolyte containing the redox shuttle molecule. The primary role of the dye SAM is to sensitize the TiO₂ semiconductor, similar to sensitization of silver halides in paper photography. Upon illumination, the dye goes into a photoexcited state and can inject an electron into the conduction band of the semiconductor. The oxidized dye is regenerated by a hole conductor, traditionally a liquid electrolyte covering the dye and containing a redox mediator. The molecular dye film has also a secondary function: it must act as an electronic barrier that prevents the photoinjected electrons to recombine with the oxidized form of the redox mediator present in the electrolyte. For typical dye molecules, this is ensured by hydrophobic alkyl chains that hinder the redox-mediator from accessing the semiconductor surface, and prevent lateral aggregation of dye molecules. The anchoring groups of the dye, usually carboxylic acids, are hydrophilic, which gives the dye an amphiphilic character and behavior often similar to anionic surfactants. The DSC macroscopic efficiency is known to depend on both the molecular arrangement of the adsorbed dye layer and the contacting electrolyte. This is generally true for most SAM-functionalized surfaces, which requires linking *in-situ* molecular-level details with macroscopic observations in order to derive a full understanding.¹²

Practically, gaining *in-situ* information about the molecular arrangement of dye-sensitizers often proves challenging. Fourier transform infrared spectroscopy was successfully used to observe the binding of dye molecules to the TiO₂ surface of DSCs.^{9,13} The average orientation of adsorbed molecules relative to the surface could be derived from combined near-edge x-ray absorption fine structure spectroscopy (NEXAFS) and photoelectron spectroscopy (PES).¹⁴⁻¹⁶ However, the irregular mesoporous titania surface prevents averaging techniques from capturing

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3 local molecular details. Scanning probe techniques can in principle overcome this difficulty and
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5 provide direct, local information about the adsorbed layer. Scanning tunneling microscopy
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7 studies in ultra-high vacuum achieved the first sub-molecular resolution images of the dye layer,
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9 but the measurements were conducted far from the functional conditions of a DSC.^{17,18} *Ex-situ*
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11 atomic force microscopy (AFM) results indicated the existence of large dye aggregates on the
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13 flat TiO₂ substrate for standard device preparation procedure, but molecular resolution was not
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15 achieved.¹⁹
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19 Recently developments in the field of AFM have made it possible to achieve sub-nanometer
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21 mapping of soft and hard surfaces in solution paving the way for *in-situ* local observations of a
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23 functional DSC's surface.²⁰⁻²²
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27 Here we report *in situ* molecular-level AFM images of adsorbed dye molecules at mesoporous
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29 and flat TiO₂ surfaces in a device-relevant liquid. We used the amphiphilic ruthenium complex
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31 Z907 (diphenyl-nonyl diphenyl-carboxyl dithio octaruthenium) dye (insert in Figure 2) due to its
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33 wide-spread use in DSCs, its good performance in long-term stability tests, and the fact that it is
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35 less prone to aggregation than other dyes.^{23 24} The AFM study is conducted with the sample fully
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37 immersed either in ethyl-isopropyl sulfone (EiPS), or acetonitrile (MeCN), both solvents being
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39 used for electrolytes in functional DSCs. We show that under normal conditions, the dye forms a
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41 single monolayer over the surface. The molecular conformation of the dye depends on the
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43 density coverage with domains of different molecular conformation able to coexist within the
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45 adsorbed sub-monolayer. The AFM results are complemented with measurements conducted
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47 using the quartz crystal microbalance with dissipation technique (QCM-D) so as to assess the
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49 average quantity of adsorbed molecules on the substrate with respect to coverage saturation. The
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51 experimental AFM and QCM-D results are supported by molecular dynamics (MD) simulations
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of dyes adsorbed on the (101) facet of anatase TiO_2 immersed in acetonitrile solvent.²⁵⁻²⁷ The simulations provide atomic-level insight into the density-dependent changes in the arrangement of the adsorbed Z907 molecules.

2. Methods

AFM

The AFM data were acquired on a commercial Multimode Nanoscope IIIa (Digital Instruments, now Bruker, Santa Barbara, USA) operated in amplitude-modulation. The sample and the scanning tip were fully immersed into the imaging liquid (ethyl *iso*-propyl sulfone (EiPS), or acetonitrile (MeCN), respectively). Before each experiment, the liquid cell was thoroughly washed in isopropanol and ultrapure water and subsequently dried with nitrogen. We used standard silicon nitride cantilevers (Olympus RC800 PSA, Olympus, Tokyo) with a nominal stiffness of $k_n = 0.76$ N/m. In each experiment the cantilever was driven acoustically with the liquid cell, close to its resonance frequency. Typical imaging amplitudes A were kept between 0.5nm and 1.5nm with the setpoint ratio A/A_0 as large as possible (A_0 is the free vibration amplitude in liquid). The use of relatively soft cantilevers and working amplitudes commensurate with the thickness of the sample-liquid interface allow us to exploit short-range solvation forces so as to enhance the resolution. In these particular imaging conditions, the energy dissipated by the vibrating AFM tip is not sufficient to fully remove the liquid between the tip and the sample, and the tip mainly probes the properties of the interfacial liquid at the surface of the sample.^{12,22,28} The phase contrast is then related to the local ‘wetting’ properties of

the sample, i.e. the local solvation free energy^{12,22} or, at the macroscopic level, the solid-liquid work of adhesion. In practice, imaging over the TiO₂ substrate provides a darker phase contrast than over the Z907 regions, indicating a higher affinity of the solvent for the substrate than for the dye-covered surface (Fig. 3c). If larger imaging amplitudes are used, the phase contrast then reflects mainly the mechanical properties of the sample, but working at large amplitudes is generally detrimental for resolution.²⁸

QCM-D

The quartz microbalance with dissipation technique (QCM-D) directly measures mass uptake on a sensor crystal inside a flow cell. It also allows for simultaneous detection of the viscoelastic properties of the adsorbed molecular layer. In the Q-Sense E4 instrument we are using, the quartz crystal sensor is contacted by gold electrodes, and its sensing side is coated with 67 nm of TiO₂ by the same atomic layer deposition (ALD) process that is used for coating the silicon substrates used for AFM measurements. The sensor is placed into a flow cell where its TiO₂ side can be exposed to liquid dye solution in order to measure mass change in situ. Given the molecular weight of the Z907 dye molecule, the QCM-D technique is sensitive enough to quantify sub-monolayers of adsorbed molecules on flat TiO₂ film, see Harms *et al.*²⁷ for details.

Computational methods

Classical molecular dynamics (MD) simulations were performed for different dye coverage and various packing modes and orientations. The TiO₂ surface was described by the Bandura Kubicki force field, whereas for the Z907 dye a force field was developed following the AMBER protocol.²⁹⁻³¹ Classical point charges were derived using the RESP procedure except for the

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3 carboxylic anchoring groups, whose charges were chosen in such a way as to reproduce the
4 experimental adsorption energy.^{32,33} For this purpose we used the Gaussian 09 Package.³⁴ The
5 force field was validated via full *ab initio* simulations of a single dye in vacuum. A united atom
6 OPLS force field was employed for acetonitrile.³⁵
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12 Experimental and computational studies have suggested different binding modes for Z907 and
13 similar dyes.^{9,36-38} Initial tests showed that the different binding modes (dissociative, bidentate,
14 or monodentate) hardly affect the space occupied by each dye and hence have little influence on
15 the overall packing geometries. For all studies presented here, we thus have adopted a single,
16 non-dissociative bidentate binding mode.
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24 Initial models of the system composed of two layers of anatase TiO₂ (108×113 Å² for low and
25 medium coverage and 54×56 Å² for high coverage) were constructed using Materials Studio.³⁹
26 Molecular dynamics simulations were performed with the Amber12 package using the PMEMD
27 module.²⁹
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34 Production runs of about 20 ns in the NVE ensemble were sampled after initial minimization
35 and 5 ns of equilibration in the canonical ensemble using Nose-Hoover thermostats at room
36 temperature (300 K).
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43 *Sample preparation*

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45 TiO₂ samples for AFM measurements were based on a (100) silicon wafer substrate coated
46 with titanium dioxide by atomic layer deposition from a tetrakis(dimethylamino)titanium
47 (TDMAT) precursor as described previously.⁴⁰ The TiO₂ film of 67 nm thickness was annealed
48 at 420°C and had a surface roughness of ~2.0 nm on a 4 μm AFM frame. X-ray diffraction of the
49 film showed evidence of anatase crystallites but no rutile phase, see supporting information. The
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3 Z907 pigment was dissolved in a 1:1 volumetric mixture of *tert*-butanol and acetonitrile, and a
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5 solution of 50.0 μM concentration was quantified by an absorption measurement using the
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7 published extinction coefficient of $12200 \text{ M}^{-1}\text{cm}^{-1}$; lower concentrations were obtained by
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9 dilution.²³
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12 Prior to staining, the AFM substrates were cleaned by UV-ozone for 10 min and subsequently
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14 heated for 30 min at 420°C to remove organic residuals and excess water from the TiO_2 surface.
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16 After cooling down to 70°C they were immersed into the dye solution for 30 min, rinsed in
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18 $t\text{BuOH:MeCN}$ mixture, immersed in MeCN for 30 min, stained again for 10 min, rinsed in
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20 $t\text{BuOH:MeCN}$ mixture and MeCN, and subsequently stored in MeCN in the dark.
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25 Samples destined for AFM measurements were usually transferred to EiPS as an imaging
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27 liquid. EiPS is a main constituent in non-volatile high-voltage electrolytes that are used in
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29 industrial applications of dye sensitized solar cells.^{41,42} EiPS was chosen for its relevance in DSC
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31 applications and for its low vapor pressure (compared to MeCN) making it is easier to reach
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33 stable imaging conditions at high resolution. Aside from experimental considerations, no
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35 differences could be seen in the images obtained in MeCN and EiPS (see supporting information
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37 Figure S1).
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41 42 43 3. Results 44 45 46 47

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49 **Figure 1** presents a high-resolution image of the surface of a DSC in a functionally relevant
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51 liquid. The measurement, conducted with AFM in EiPS, provides a unique insight into the sub-
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53 nanometer details of the device's surface and indicates some structure in the dye layer. The dye
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55 molecules appear to be arranged along some preferential directions (arrows in the inset) although
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no long-range order is visible. These results should however be taken cautiously due to the high surface curvature of mesoporous TiO_2 which renders AFM imaging challenging due to tip-convolution effects. An additional difficulty arises from the fact that dye molecules tend to accumulate primarily in holes and surface groves at intermediate coverage, making a study of the dye molecular arrangement as a function of surface coverage difficult.

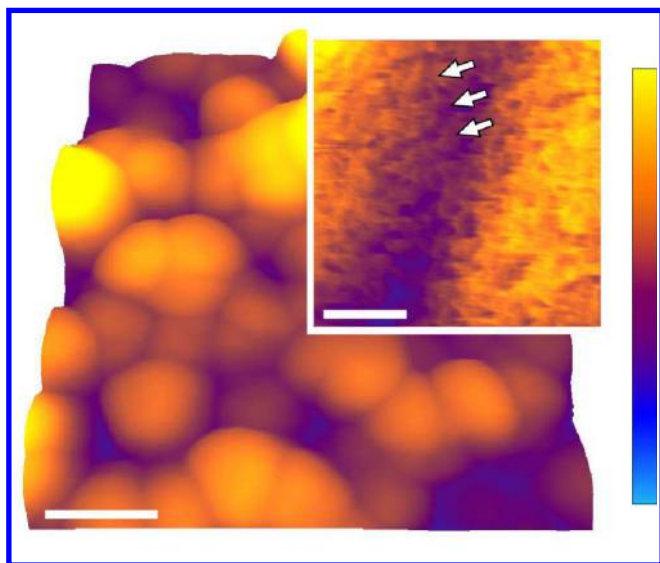


Figure 1. High-resolution AFM image of the surface of a DSC in liquid. The surface is composed of mesoporous TiO_2 stained with the Z907 ruthenium dye. The TiO_2 nanoparticles are clearly visible in the main image. The inset shows molecular detail of the dye arrangement at the edge of a nanoparticle with some ordering visible (arrows). The scale bars are 40 nm (main image) and 3 nm (inset). The colour scale is 70 nm (main image) and 6 nm (inset).

To overcome these difficulties, we have used flat TiO_2 substrates throughout this study. The substrates, obtained by atomic layer deposition, present a sufficiently low roughness on the nanoscale to avoid ambiguous interpretation of the AFM results. For each sample, the actual surface coverage is determined by QCM-D so as to ensure that the local AFM observations

reflect global surface properties. The adsorption behavior of the same Z907–TiO₂ system has previously been studied by using a QCM-D.²⁷ **Figure 2** shows the adsorption isotherm for Z907 on flat TiO₂ films. The figure uses previously published data²⁷ as a reference for comparison with the current measurements. The isotherm follows a Langmuir-type behavior (red line), indicating a saturation value of 103 ng cm⁻² area mass uptake over the concentration range on display. This corresponds to 0.76 molecules/nm², or a molecular footprint of 1.31 nm²/molecule when assuming a flat surface. We define this saturation value as 100 % mass coverage, which should correspond to a densely packed monolayer of Z907. For staining the AFM samples, dye concentrations were chosen such that a mass coverage of approximately 30 %, 60 % or 100 % was obtained (green data crosses in Figure 2).

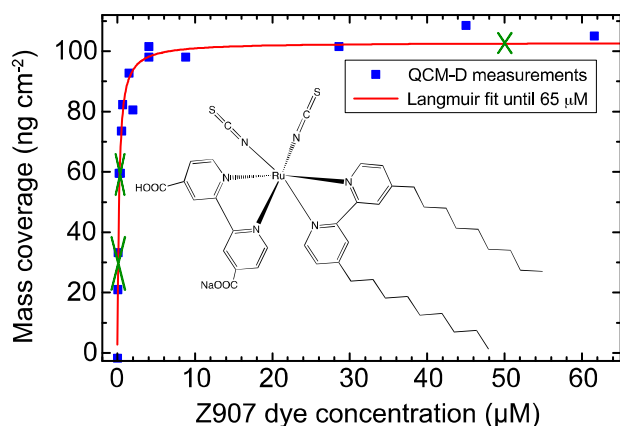


Figure 2. QCM-D area mass uptake over concentration of sensitizing dye solution with a Langmuir isotherm fitted to the data. Blue data points are taken from previously published experiments²⁷. Green crosses mark the three concentrations of dye solutions used for staining the AFM samples and indicate their corresponding mass coverage. The insert shows the structure of the Z907 ruthenium dye.

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3 A representative AFM topographic image of the flat TiO₂ surface after sensitization with dye
4 molecules (30 % mass coverage) is shown in **Figure 3a**. The image shows large protrusions (20-
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7 30 nm wide, and ~2 nm high) that are related to the roughness of the TiO₂ substrate. Details of
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9 the dye molecules are already visible, appearing as a sub-nanometer, mostly homogeneous
10 roughness on the surface. This is confirmed in higher magnification images of the sample where
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12 the dye film appears as homogenous sponge-like structure (inset in Figure 3a). Using harsh
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14 imaging conditions, it is possible to mechanically remove dye molecules in selected regions by
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16 scratching. The scratched region, which corresponds to the TiO₂ substrate, appears darker in the
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18 phase image (purple arrow in Figure 3b and c). This phase contrast indicates a higher affinity of
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20 the solvent for the TiO₂ than for the dye, and could be consistently used throughout this study to
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22 identify dye-covered (light) and uncovered (dark) regions.^{12,22} At 30 % mass coverage, the dye
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24 layer exhibits dark spots in the phase, suggesting that uniform gaps exist between the adsorbed
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26 Z907 molecules. These gaps give the apparent sponge-like appearance to the dye layer
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28 topography. The thickness of the dye film is difficult to evaluate directly from Figure 3a due to
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30 the roughness of the substrate. It is however possible to use the exposed TiO₂ region as a
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32 reference. A line profile taken at the edge of the dye layer indicates a thickness of ~0.6 nm
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34 (Figure 3d). This value is a lower estimate of the real thickness due to the mechanical
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36 perturbation induced by the AFM tip on the dye molecules during the imaging process.
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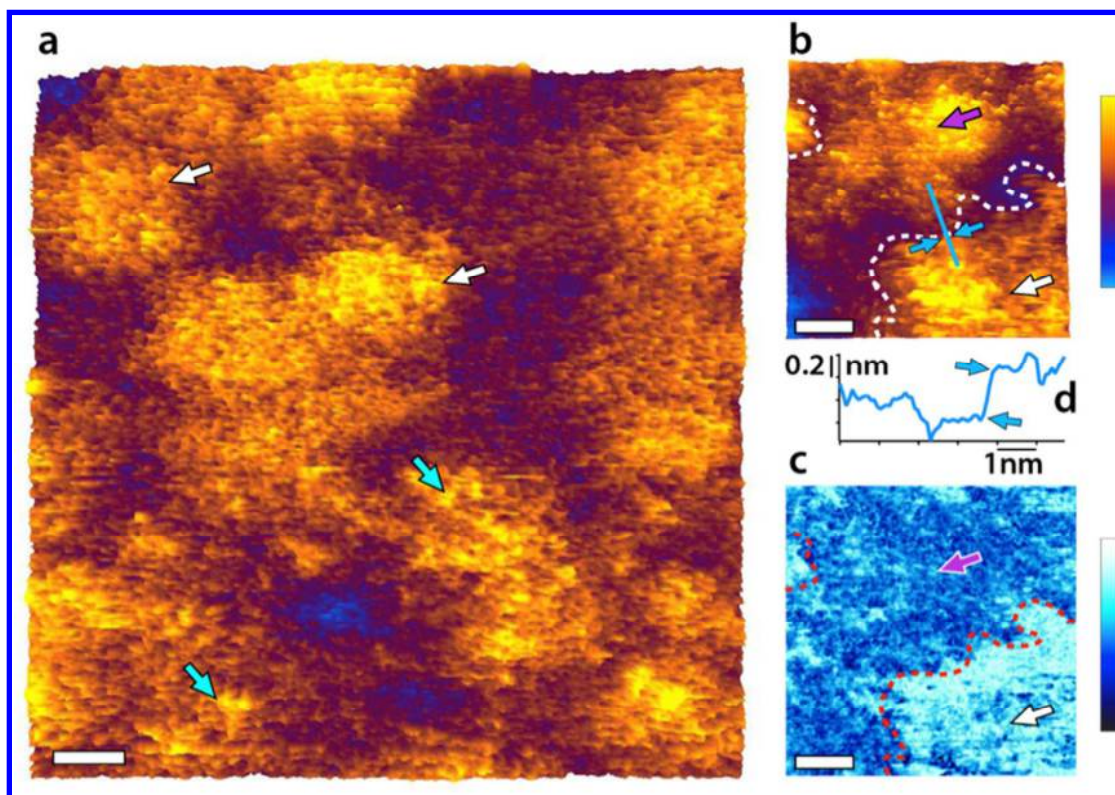


Figure 3. AFM micrographs of a TiO_2 surface covered with Z907 ruthenium dye (30 % mass coverage). (a) A low magnification (100 nm) topographic image shows almost uniform coverage by the dye apart for a few higher dye domains (blue arrows). The ~ 20 nm wide protrusions (white arrows) are related to the substrate roughness. Higher resolution topographic (b) and phase (c) images of the surface reveal a sponge-like structure of the dye layer (white arrow). The substrate can also be exposed by scratching with the AFM tip (b-c) revealing a ~ 0.6 nm dye layer thickness. The exposed TiO_2 substrate (purple arrow) exhibit a clear phase contrast (dotted red line) with the lighter Z907 domains. A topographic profile (d) taken over the TiO_2 -Z907 border (blue line in b) indicates a thickness of ~ 0.4 nm for the Z907 dye layer. The topographic images are always represented with an orange-blue color scale and the phase images in blue-black throughout the paper. The scale bars are 10 nm (a) and 3 nm (b, c). The colour bars are 3 nm (a, b) and 15° (c).

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6 A closer look at Figure 3a reveals occasional variations in height of the dye layer over flat
7 substrate regions (blue arrows). These regions hint to local variations of the Z907 molecular
8 arrangement on the substrate surface, which could be related to the density of dye molecules. In
9 order to examine this effect in a systematical manner, we acquired high-resolution AFM images
10 of the dye layer at different mass coverage, as determined by QCM-D.
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18 Representative AFM images are presented in **Figure 4** for 0 %, 30 %, 60 % and 100 % mass
19 coverage. A clear trend is visible in both the topography and the phase with the increase of dye
20 coverage. The bare substrate (0 %) appears relatively rough, the image is noisy and provides
21 little phase contrast. At 30 % mass coverage, 1-3 nm wide dye features are visible in both
22 topography and the phase, and form a soft sponge-like layer probably templated by the atomic
23 structure of the TiO₂ substrate. From the phase image, the holes (red arrow) can be attributed to
24 the substrate while the top of the layer is due to dye molecules and appear already more regular
25 and smoother than raw substrate (white arrow). At 60 % mass coverage, the layer is more
26 ordered and appears in an intermediate situation with the dye molecules forming both rows
27 (white arrow) and lower, less ordered regions (green arrow). The fully covered surface appears
28 smooth with little height variations. The whole surface is covered in row-like domains, which are
29 not necessarily aligned (arrows). The phase image becomes consistently brighter as the surface
30 coverage increases, indicating the substrate is fully covered at 100 % mass coverage.
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48 Interestingly, the dye molecules always spread over all the space available and never form
49 isolated islands. At 10 % mass coverage, the spreading of the dye molecules prevented non-
50 destructive imaging (not shown).
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The AFM results suggest a change in the molecular arrangement of the dye molecules on the surface as the dye coverage increases. The coexistence of two height levels at intermediate coverage supports this explanation. The formation of dye rows at higher coverage (also visible in MeCN, see supplementary Figure S1) is consistent with the observations on the mesoporous TiO₂ (Figure 1) and coincide with an increased layer thickness, suggesting that the Z907 molecules sit with their alkyl chains extended away from the substrate surface when arranged in rows (Figure 7). This interpretation would also explain the increased surface density of dye at higher mass coverage, especially given the fact that the dye molecules spread over the whole available TiO₂ at all coverage conditions.

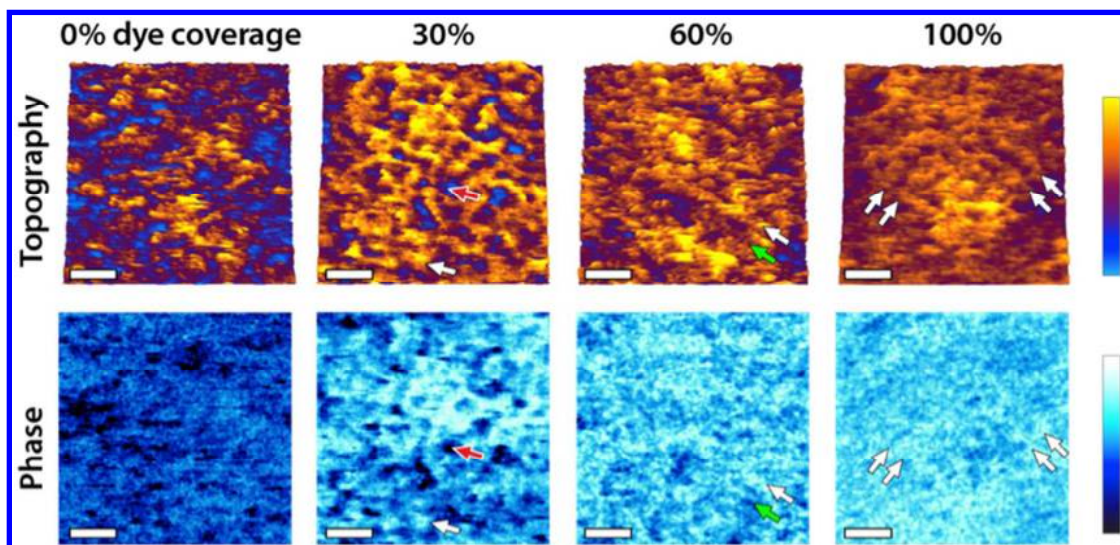


Figure 4. High-resolution AFM images of the dye layer at 0 %, 30 %, 60 % and 100 % mass coverage obtained in similar imaging conditions. At 0 % the substrate appears rough and noisy due to short-range tip-sample attractive interactions. At 30 %, the dye molecules (white arrow) assemble in a soft sponge-like disordered structure that can easily be disrupted by the AFM tip. Multiples holes are visible in the layer (red arrow) and appear darker in the phase. At 60 %, the layer is partially ordered with the apparition of rows (white arrow) and less ordered lower

regions (green arrow). At 100 % the surface is fully covered, it appears smooth and only dye rows are visible (white arrows). The scale bar is 2 nm and the colour scales are 1 nm (topography) and 15° in all images.

To further explore the atomistic arrangement of the dye film on the TiO₂ surface, we performed molecular dynamics (MD) simulations at different dye densities. 100 % mass coverage was simulated using a density of 0.76 molecules/nm² as obtained from QCM-D measurements. The dye molecules were arranged on a crystalline anatase (101) TiO₂ slab with two layers. Possible binding locations were identified based on geometric arguments: using an approximate distance between the two carboxylic groups of a bipyridine moiety of ca. 7 Å as a gauge, we tried to find adsorbing sites on the substrate with the same distance. Five possible locations were identified, as displayed in **Figure 5**. The same 5 locations were confirmed by random adsorption simulations where dyes initially located at 10-15 Å distance from the surface in vacuum were allowed to adsorb randomly during the first nanosecond of the simulation. For each of the five binding locations, a regular system of 25 dyes adsorbed on the titanium oxide surface was constructed. After minimization, the lowest energy configuration (Site 1 in **Table 1**) was chosen for conducting further simulations to study the effect of coverage density on packing.

As a further validation, we performed annealing simulations of all 5 systems, in which the temperature was raised to 600 K followed by cooling down to low temperatures. Consistent with the relative energetics shown in Table 1, dyes located in the energetically most stable site 1 arrangement remained at their binding sites, whereas other configurations went through several transitions between different arrangements, (for configurations with sites 5, 2, and 4) and occasionally detached from the surface (in the case of site 3). An additional parameter that

strongly influences the energetics of the packing is the orientation of the dye. For instance in the most stable orientation for site 1, the sulfur atoms are inversely aligned along the $[10\bar{1}]$ direction, whereas the opposite orientation is less stable (see supporting information Figure S2).

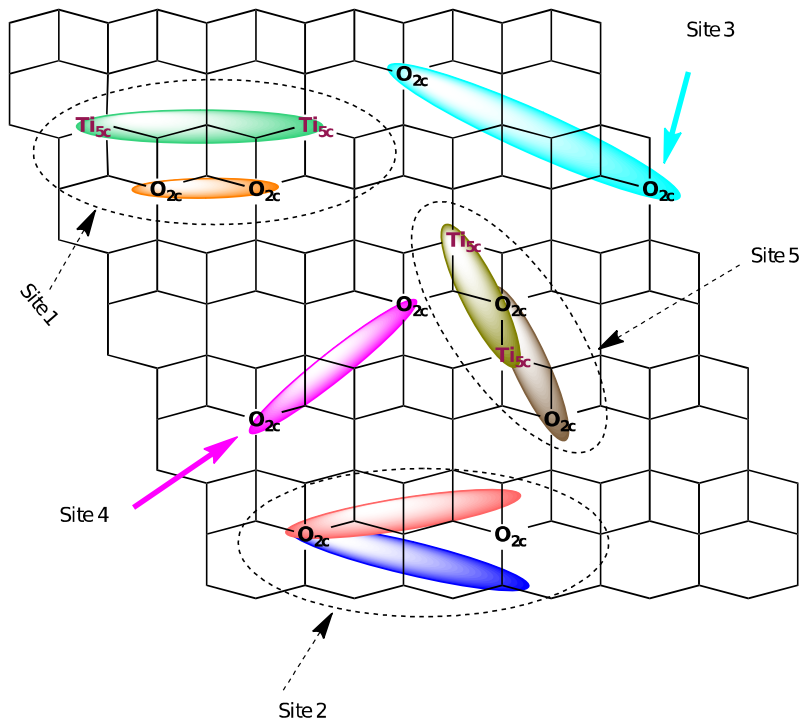


Figure 5. Five possible location sites suitable for simultaneous anchoring of the carboxygroups of the bipyridine moiety. The Z907 dye always occupies roughly the same (dotted) area in sites 1, 2 and 5, regardless of the selected binding mode inside the ellipse. For site 1, Z907 in its fully protonated structure can make hydrogen bonds with two 2-coordinated oxygens (O_{2c}). In its deprotonated state, the bipyridine moiety can make bonds to 5-coordinated Ti (Ti_{5c}), either way occupying the same space shown in dots. The same holds true for site 5. For site 2, the bipyridine can be in the salmon-colored ellipse or the blue one, either way making hydrogen bonds to the same two ridge oxygens indicated.

Table 1. Relative energetics for different dye location sites, as displayed in Figure 5, evaluated for a system composed of 25 dyes. The relative energetics was evaluated for a 33% mass coverage system where dye-dye interactions are less important.

Adsorption site	Relative energetics [kcal/mol dye molecule]
Site 1	0
Site 2	15.4
Site 3	25.6
Site 4	30.8
Site 5	48.7

In order to visualize the effect of dye coverage on the conformation of the dye layer, we computed a topographic picture of the system comprising 25 dye molecules averaged over 20 ns of simulation (**Figure 6**), comparing 33 % mass coverage ($0.23 \text{ molecules nm}^{-2}$), 66 % mass coverage ($0.51 \text{ molecules nm}^{-2}$) and 100 % mass coverage ($0.76 \text{ molecules nm}^{-2}$). In order to change the mass coverage in the computations, the size of the TiO_2 slab was adjusted accordingly, while the number of dye molecules was kept constant. At lower densities, one of the lipophilic alkyl chains is mostly extended parallel to the surface whereas the other is pointing upwards (**Figure 7**). This leads to a configuration where the dyes are packed closer to the surface, i.e. the average layer distance is ca. 8.7 \AA with an average tilting angle of $38^\circ \pm 6^\circ$ of the bipyridine moiety with respect to the titanium oxide surface. Figure 7 shows that for 100 % dye coverage, the atomic density profile along the z direction has a shoulder around 13 \AA and the

probability to find dye atoms (mostly from the alkyl chains) in this range (13-25 Å) is higher than the one of the 33 % mass coverage system (bottom graph in Figure 7). In fact, at higher densities (66 % and 100 %), both alkyl chains of each dye molecule start to be oriented vertically with respect to the TiO₂ surface with average dye-layer thicknesses of approximately 9.00 Å and 10.2 Å and an average tilting angle of $42^{\circ} \pm 3^{\circ}$ and $55^{\circ} \pm 3^{\circ}$, respectively (Figure 7-note that instantaneous tilting angles shown in the figure for one snapshot are not necessarily identical to the average values).

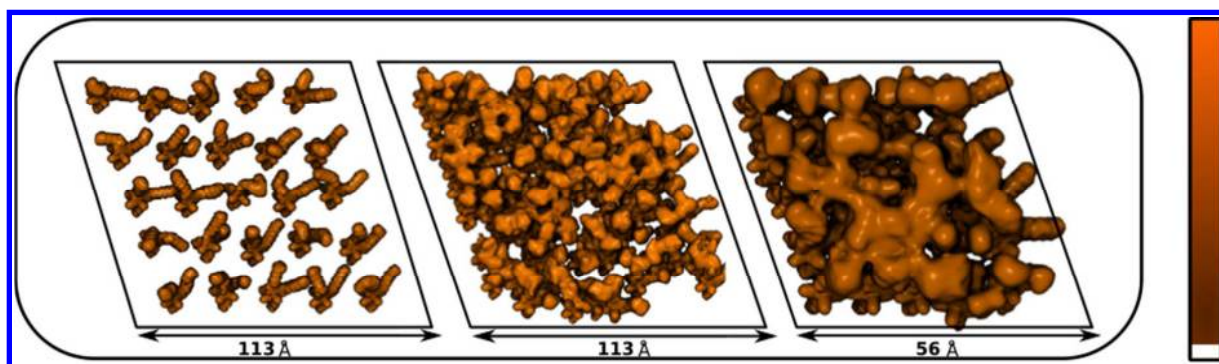


Figure 6 . The simulated AFM pictures for different mass coverage (33%, 66%, and 100% from left to right, respectively). Map of the weighted atomic density of dye molecules. The map is done by replacing each dye atom with a normalized Gaussian distribution of width (standard deviation) equal to the atomic radius. The Gaussian distribution for each atom is then weighted with the occupancy. The various Gaussians are added and distributed on a grid (orange color). The isosurface value is 0.01. The same map with restriction to the parts of dye molecules that are 13-25 Å away from the TiO₂ surface is shown in the supporting information Figure S7.

As the experimental results in this AFM study and in other STM studies³⁷ suggest, the TiO₂ surface templates the dye arrangement via the binding site, and the packing is less driven by dye-dye interactions in terms of energy. Simulations results for the low coverage system (less dye-dye interactions) also show significant energy differences between different dye arrangements on the TiO₂ template (Table 1). AFM nanographs at 60 % mass coverage suggest the possible coexistence of distinct domains of dye molecules with the alkyl chains either pointing away from the surface, or stretched out along the surface. Indeed our MD simulations results also reflect the coexistence of quasi parallel and quasi vertical alkyl chains and also show that the relative population of the two alkyl chain orientations is density dependent (Figure 7). At low coverage one alkyl chain is mostly parallel and one vertical while at high coverage both alkyl chains are found in a quasi vertical configuration. The intermediate coverage consists of a mixture of dye molecules with these two main configurations. For this intermediate coverage range, we also explored few inhomogeneous configurations with dye domain formation (supporting information Figure S3).

In addition, we analyzed the solvent accessibility of the SAM (supporting information Figure S4). For all three coverages, the dye molecules reduce the accessibility of the solvent to the TiO₂ with respect to a dye-free surface (left side on Figure S4). This solvent screening sets in at farer distances and is more effective for higher coverage where alkyl chains are positioned more vertically and the monolayer thickness is larger.

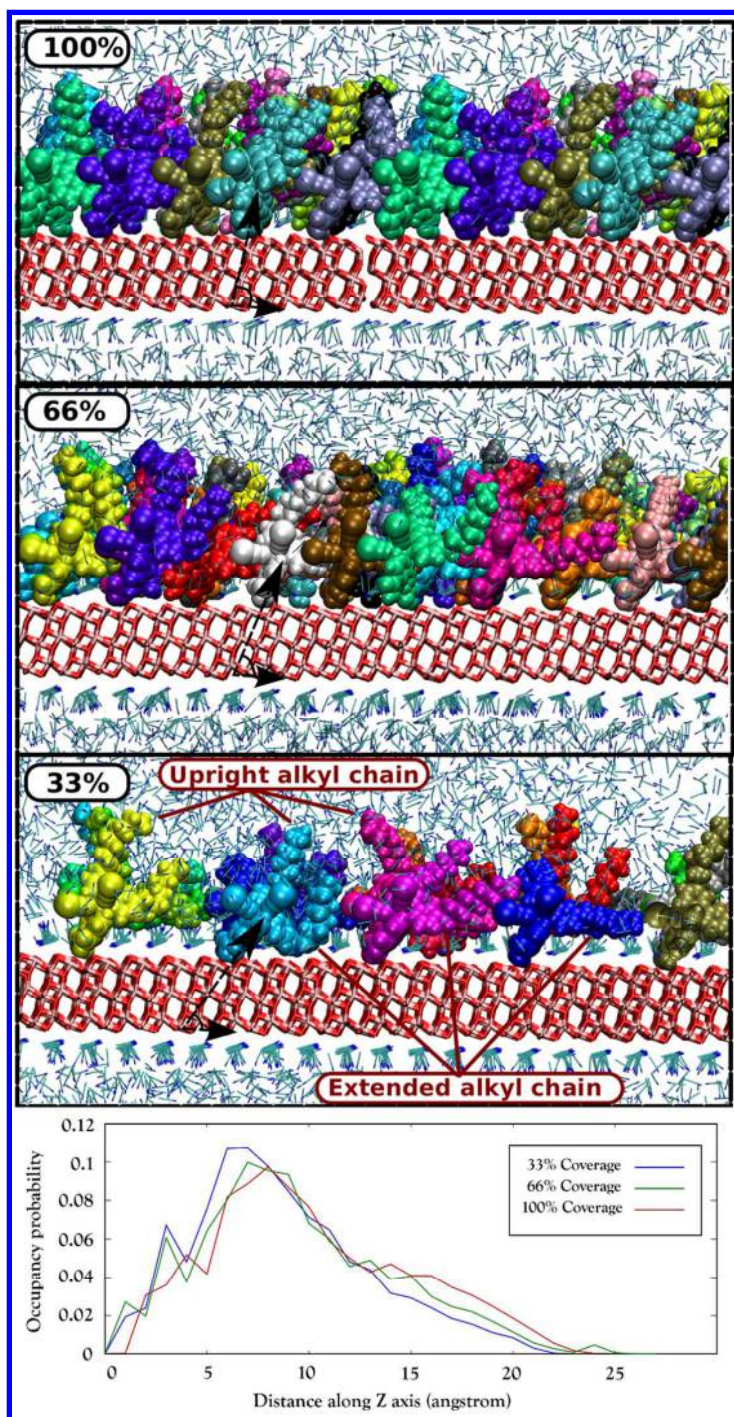


Figure 7. Side view of the three systems with different mass coverage. The tilting angle is indicated with black arrows. When going to higher mass coverage (top pictures), more alkyl chains assume an upright position. Lower part: The probability of finding dye atoms along the Z-axis (normal to the surface) for 20 ns of MD simulation in NVE ensemble.

Besides the conformational change of the alkyl chains with respect to the surface, MD simulations at nominal 100 % dye coverage also indicate that the binding location of the molecules close to maximum coverage can be altered. In the areas with densely packed arrangements, dyes encumber each other forcing their neighbors to take positions, which are not usually energetically preferred (in terms of adsorption sites and can even detach from the surface at higher temperatures (supporting information Figure S5).

4. Discussion

Results from AFM measurements and MD computations both indicate that the amphiphilic Z907 dye covers most of the TiO_2 surface already at 33 % mass coverage by stretching out its alkyl chains along the TiO_2 surface. For 100 % weight coverage, experiment and simulation show that the molecules form a densely packed monolayer, with both alkyl chains adapting an upright conformation. This microscopic observation confirms the common understanding that alkyl chains can shield the TiO_2 surface in applications like dye sensitized solar cells and it elucidates the way in which they do.

Our observation of two different types of conformation of the dye molecules matches well with previous findings on anisotropic dye molecules by combined NEXAFS and PES studies;^{16,43} our measurement offers an independent confirmation by a direct and complementary AFM observation in an actually relevant liquid environment. The existence of two adsorbed conformations is reminiscent of the well-known ‘flat lying’ and ‘standing’ molecular configurations of alkanethiols SAMs on gold.⁴⁴ The analogy with the present case is nonetheless

not obvious given the important differences in the type of bond formed between the dye and the substrate.

Our measurements also provide high-resolution lateral information, i.e. conformity and homogeneity of the film at high mass coverage. Considering the amphiphilic nature of the Z907 molecule, these findings could remain valid for surfactant adsorption at low concentration in general.

In the particular case of dye sensitized solar cells, the staining of mesoporous TiO_2 is carried out at high Z907 dye concentration (250 μM). However, it is known that it takes several hours for the dye to reach the bottom of a mesoporous film, and even longer to fully saturate the dye uptake in the mesoporous film.^{45,46} This indicates that during the staining process, all of the different conformations and different degrees of mass coverage are present in part of the mesoporous TiO_2 film. This implies that the results derived by QCM-D and AFM on flat model systems provide meaningful insights that are relevant to the mesoporous system. In particular, amphiphilic sensitizers can effectively cover the TiO_2 surface already at low mass coverage, so the shielding of the TiO_2 from the electrolyte can be effective even if the staining of deeper layers of the mesoporous TiO_2 film is incomplete. Practically, this would result in a working device with good fill factor and photovoltage, but the photocurrent would be inferior to a similar device in which 100% dye mass coverage was achieved. On both, flat and mesoporous TiO_2 , we consistently observe monolayers of Z907, not agglomerations, as earlier AFM reports of lower resolution suggest.¹⁹ We observed dye agglomerations only upon special sample preparation procedures, e.g. when the rinsing of the sample was omitted. Furthermore, the existence of molecular rows could be observed on both the flat and the mesoporous substrate by AFM in EiPS, supporting the generality of our findings in different electrolytes. The observation of two

different conformations is in fact further supported by the two-step adsorption kinetics that are often observed in DSCs.^{27,47}

In the more general sense, it is very encouraging that the computational method produces good agreement with the results of the AFM study. The MD simulation only used the quantitative input on the number of dye molecules per area, as obtained experimentally from the QCM-D mass coverage. Computations then produced a detailed description of the adsorbed molecular film in liquid environment, which corresponds very well to the experimental data obtained independently by AFM. The AFM study presented in this paper is at the limit of the resolution that can currently be achieved on molecular films in a relevant liquid environment, but the model at the basis of the MD simulation may still describe the behavior of molecular films correctly at a level that is beyond the resolution of current experimental methods.

5. Conclusion

In this study we have combined high-resolution AFM, QCM-D and MD simulations to elucidate the molecular arrangement of the Z907 dye molecules at the surface of TiO₂ in a functionally relevant liquid. Our results detail the formation of the dye monolayer, showing several molecular conformations on the surface at different dye concentration.

Future work will address molecular films that consist of functional molecules coadsorbed with chelating agents such as bile acids, e.g. porphyrin sensitizers and cheno deoxycholic acid, where the nature of interaction and the arrangement of dye and coadsorbate within the sensitizing film still wait to be unveiled.

Supporting Information. High-resolution AFM image of the Z907 dye layer in acetonitrile. orientation with respect to the crystal lattice of packing, calculated solvent density along the z axis (vertical to the TiO₂ slab). This material is available free of charge via the Internet at <http://pubs.acs.org>

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REFERENCES

- (1) Akkerman, H. B.; Blom, P. W. M.; de Leeuw, D. M.; de Boer, B. Towards Molecular Electronics with Large-Area Molecular Junctions. *Nature* **2006**, *441*, 69–72.
- (2) Bain, C. D.; Whitesides, G. M. Correlations Between Wettability and Structure in Monolayers of Alkanethiols Adsorbed on Gold. *J. Am. Chem. Soc.* **1988**, *110*, 3665–3666.
- (3) Flink, S.; Van Veggel, F.; Reinhoudt, D. N. Sensor Functionalities in Self-Assembled Monolayers. *Adv. Mater.* **2000**, *12*, 1315-1328.
- (4) Langer, R.; Tirrell, D. A. Designing Materials for Biology and Medicine. *Nature* **2004**, *428*, 487–492.
- (5) O'Regan, B.; Grätzel, M. A Low-Cost, High-Efficiency Solar Cell Based on Dye-Sensitized Colloidal TiO₂ Films. *Nature* **1991**, *353*, 737–740.
- (6) Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G. Self-Assembled Monolayers of Thiolates on Metals as a Form of Nanotechnology. *Chem. Rev.* **2005**, *105*, 1103-1169.

- (7) Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. Dye-Sensitized Solar Cells. *Chem. Rev.* **2010**, *110*, 6595–6663.
- (8) Han, L.; Islam, A.; Chen, H.; Malapaka, C.; Zhang, S.; Yang, X.; Yanagida, M. High-Efficiency Dye-Sensitized Solar Cell with a Novel Co-Adsorbent. *Energy Environ. Sci.* **2012**, *5*, 6057–6060.
- (9) Gao, F.; Wang, Y.; Shi, D.; Zhang, J.; Wang, M.; Jing, X.; Humphry-Baker, R.; Wang, P.; Zakeeruddin, S. M.; Grätzel, M. Enhance the Optical Absorptivity of Nanocrystalline TiO₂ Film with High Molar Extinction Coefficient Ruthenium Sensitizers for High Performance Dye-Sensitized Solar Cells. *J. Am. Chem. Soc.* **2008**, *130*, 10720–10728.
- (10) Grätzel, M. The Advent of Mesoscopic Injection Solar Cells. *Prog. Photovolt: Res. Appl.* **2006**, *14*, 429–442.
- (11) Yella, A.; Lee, H. W.; Tsao, H. N.; Yi, C.; Chandiran, A. K.; Nazeeruddin, M. K.; Diau, E. W. G.; Yeh, C. Y.; Zakeeruddin, S. M.; Grätzel, M. Porphyrin-Sensitized Solar Cells with Cobalt (II/III)-Based Redox Electrolyte Exceed 12 Percent Efficiency. *Science* **2011**, *334*, 629–634.
- (12) Kuna, J. J.; Voitchovsky, K.; Singh, C.; Jiang, H.; Mwenifumbo, S.; Ghorai, P. K.; Stevens, M. M.; Glotzer, S. C.; Stellacci, F. The Effect of Nanometre-Scale Structure on Interfacial Energy. *Nat. Mater.* **2009**, *8*, 837–842.
- (13) Schiffmann, F.; VandeVondele, J.; Hutter, J.; Wirz, R.; Urakawa, A.; Baiker, A. Protonation-Dependent Binding of Ruthenium Bipyridyl Complexes to the Anatase(101) Surface. *J. Phys. Chem. C* **2010**, *114*, 8398–8404.

(14) Yu, S.; Ahmadi, S.; Zuleta, M.; Tian, H.; Schulte, K.; Pietzsch, A.; Hennies, F.; Weissenrieder, J.; Yang, X.; Göthelid, M. Adsorption Geometry, Molecular Interaction, and Charge Transfer of Triphenylamine-Based Dye on Rutile TiO₂(110). *J. Chem. Phys.* **2010**, *133*, 224704.

(15) Marinado, T.; Hahlin, M.; Jiang, X.; Quintana, M.; Johansson, E. M. J.; Gabrielsson, E.; Plogmaker, S.; Hagberg, D. P.; Boschloo, G.; Zakeeruddin, S. M.; Grätzel, M.; Siegbahn, H.; Sun, L.; Hagfeldt, A.; Rensmo, H. Surface Molecular Quantification and Photoelectrochemical Characterization of Mixed Organic Dye and Coadsorbent Layers on TiO₂ for Dye-Sensitized Solar Cells. *J. Phys. Chem. C* **2010**, *114*, 11903–11910.

(16) Rienzo, A.; Mayor, L. C.; Magnano, G.; Satterley, C. J.; Ataman, E.; Schnadt, J.; Schulte, K.; O'Shea, J. N. X-Ray Absorption and Photoemission Spectroscopy of Zinc Protoporphyrin Adsorbed on Rutile TiO₂(110) Prepared by in Situ Electrospray Deposition. *J. Chem. Phys.* **2010**, *132*, 084703.

(17) Kley, C. S.; Dette, C.; Rinke, G.; Cechal, J.; Jung, S. J.; Baur, M.; Dürr, M.; Rauschenbach, S.; Giustino, F.; Stepanow, S.; Kern, K. Atomic-Scale Observation of Multiconformational Binding and Energy Level Alignment of Ruthenium-Based Photosensitizers on TiO₂ Anatase. *Nano Lett.* **2014**, *14*, 563-569.

(18) Sasahara, A.; Fujio, K.; Koide, N.; Han, L.; Onishi, H. STM Imaging of a Model Surface of Ru(4,4''-Dicarboxy-2,2''-Bipyridine)₂(NCS)₂ Dye-Sensitized TiO₂ Photoelectrodes. *Surf. Sci.* **2010**, *604*, 106–110.

(19) Marquet, P.; Andersson, G.; Snedden, A.; Kloo, L.; Atkin, R. Molecular Scale Characterization of the Titania - Dye - Solvent Interface in Dye-Sensitized Solar Cells. *Langmuir* **2010**, *26*, 9612–9616.

(20) Fukuma, T.; Higgins, M. J.; Jarvis, S. P. Direct Imaging of Lipid-Ion Network Formation Under Physiological Conditions by Frequency Modulation Atomic Force Microscopy. *Phys. Rev. Lett.* **2007**, *98*, 106101.

(21) Fukuma, T.; Ueda, Y.; Yoshioka, S.; Asakawa, H. Atomic-Scale Distribution of Water Molecules at the Mica-Water Interface Visualized by Three-Dimensional Scanning Force Microscopy. *Phys. Rev. Lett.* **2010**, *104*, 016101.

(22) Voitchovsky, K.; Kuna, J. J.; Contera, S. A.; Tosatti, E.; Stellacci, F. Direct Mapping of the Solid–Liquid Adhesion Energy with Subnanometre Resolution. *Nat. Nanotechnol.* **2010**, *5*, 401–405.

(23) Zakeeruddin, S. M.; Nazeeruddin, M. K.; Humphry-Baker, R.; Pechy, P.; Quagliotto, P.; Barolo, C.; Viscardi, G.; Grätzel, M. Design, Synthesis, and Application of Amphiphilic Ruthenium Polypyridyl Photosensitizers in Solar Cells Based on Nanocrystalline TiO₂ Films. *Langmuir* **2002**, *18*, 952–954.

(24) Wang, P.; Zakeeruddin, S. M.; Moser, J. E.; Nazeeruddin, M. K.; Sekiguchi, T.; Grätzel, M. A Stable Quasi-Solid-State Dye-Sensitized Solar Cell with an Amphiphilic Ruthenium Sensitizer and Polymer Gel Electrolyte. *Nat. Mater.* **2003**, *2*, 402–407.

(25) Rodahl, M.; Hook, F.; Krozer, A.; Brzezinski, P.; Kasemo, B. Quartz Crystal Microbalance Setup for Frequency and Q-Factor Measurements in Gaseous and Liquid Environments. *Rev. Sci. Instrum.* **1995**, *66*, 3924–3930.

(26) Rodahl, M.; Kasemo, B. Frequency and Dissipation-Factor Responses to Localized Liquid Deposits on a QCM Electrode. *Sens. Actuators, B* **1996**, *37*, 111–116.

(27) Harms, H. A.; Tétreault, N.; Gusak, V.; Kasemo, B.; Grätzel, M. In-Situ Investigation of Dye Adsorption on TiO₂ Films Using a Quartz Crystal Microbalance with Dissipation Technique. *Phys. Chem. Chem. Phys.* **2012**, 9037–9040.

(28) Voïtchovsky, K. Phys. Rev. E Anharmonicity, solvation forces, and resolution in atomic force microscopy at the solid-liquid interface. *Phys. Rev. E* **2013**, *88*, 022407.

(29) Cornell, W. D.; Cieplak, P.; Bayly, C. I.; Gould, I. R.; Merz, K. M.; Ferguson, D. M.; Spellmeyer, D. C.; Fox, T.; Caldwell, J. W.; Kollman, P. A. [AMBER] a Second Generation Force Field for the Simulation of Proteins, Nucleic Acids, and Organic Molecules. *J. Am. Chem. Soc.* **1995**, *117*, 5179–5197.

(30) Bandura, A. V.; Kubicki, J. D. Derivation of Force Field Parameters for TiO₂ - H₂O Systems From Ab Initio Calculations. *J. Phys. Chem. B* **2003**, *107*, 11072–11081.

(31) Case, D. A.; Darden, T. A.; Cheatham, T. E., III; Simmerling, C. L. AMBER 12 - Amber Package. *University of California* **2012**.

(32) Bayly, C. I.; Cieplak, P.; Cornell, W.; Kollman, P. A. A Well-Behaved Electrostatic Potential Based Method Using Charge Restraints for Deriving Atomic Charges: the RESP Model. *J. Phys. Chem.* **1993**, *97*, 10269–10280.

(33) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G. Gaussian 09, revision A. 1. *Gaussian Inc., Wallingford, CT* **2009**.

(34) Sushko, M. L.; Gal, A. Y.; Shluger, A. L. Interaction of Organic Molecules with the TiO₂ (110) Surface: Ab Initio Calculations and Classical Force Fields. *J. Phys. Chem. B* **2006**, *110*, 4853–4862.

(35) Jorgensen, W. L.; Tirado-Rives, J. The OPLS [Optimized Potentials for Liquid Simulations] Potential Functions for Proteins, Energy Minimizations for Crystals of Cyclic Peptides and Crambin. *J. Am. Chem. Soc.* **1988**, *110*, 1657–1666.

(36) Pastore, M.; Angelis, F. D. First-Principles Computational Modeling of Fluorescence Resonance Energy Transfer in Co-Sensitized Dye Solar Cells. *J. Phys. Chem. Lett.* **2012**, *3*, 2146–2153.

(37) Grinter, D. C.; Nicotra, M.; Thornton, G. Acetic Acid Adsorption on Anatase TiO₂ (101). *J. Phys. Chem. C* **2012**, *116*, 11643–11651.

(38) Polander, L. E.; Yella, A.; Curchod, B. F. E.; Ashari Astani, N.; Teuscher, J.; Scopelliti, R.; Gao, P.; Mathew, S.; Moser, J. E.; Tavernelli, I.; Rothlisberger, U.; Grätzel, M.; Nazeeruddin, M. K.; Frey, J. Towards Compatibility Between Ruthenium Sensitizers and Cobalt Electrolytes in Dye-Sensitized Solar Cells. *Angew. Chem. Int. Ed.* **2013**, *52*, 8731–8735.

(39) Accelrys Software Inc., Discovery Studio Modeling Environment, Release 4.0, *San Diego: Accelrys Software Inc.*, **2013**.

(40) Tétreault, N.; Heiniger, L.-P.; Stefik, M.; Labouchère, P. L.; Arsenault, É.; Nazeeruddin, N. K.; Ozin, G. A.; Grätzel, M. Atomic Layer Deposition for Novel Dye-Sensitized Solar Cells. *ECS Transactions* **2011**, *41*, 303-314.

(41) Yanada, K.; Chiba, K.; Yamaguchi, Y.; Yamamoto, H. Characteristics of Dye-Sensitized Solar Cells Using Linear Sulfones as an Electrolyte Solvent. *Electrochim. Acta* **2012**, *79*, 163–167.

(42) Chiba, K.; Ueda, T.; Yamaguchi, Y.; Oki, Y.; Saiki, F.; Naoi, K. Electrolyte Systems for High Withstand Voltage and Durability II. Alkylated Cyclic Carbonates for Electric Double-Layer Capacitors. *J. Electrochem. Soc.* **2011**, *158*, A1320.

(43) Hahlin, M.; Johansson, E. M. J.; Plogmaker, S.; Odelius, M.; Hagberg, D. P.; Sun, L.; Siegbahn, H.; Rensmo, H. Electronic and Molecular Structures of Organic Dye/TiO₂ Interfaces for Solar Cell Applications: a Core Level Photoelectron Spectroscopy Study. *Phys. Chem. Chem. Phys.* **2010**, *12*, 1507.

(44) Schwartz, D. K. Mechanisms and Kinetics of Self-Assembled Monolayer Formation. *Annu. Rev. Phys. Chem.* **2001**, *52*, 107–137.

(45) O'Regan, B.; Xiaoe, L.; Ghaddar, T. Dye Adsorption, Desorption, and Distribution in Mesoporous TiO₂ Films, and Its Effects on Recombination Losses in Dye Sensitized Solar Cells. *Energy Environ. Sci.* **2012**, *5*, 7203–7215.

(46) Gusak, V.; Heiniger, L.-P.; Graetzel, M.; Langhammer, C.; Kasemo, B. Time-Resolved Indirect Nanoplasmonic Sensing Spectroscopy of Dye Molecule Interactions with Dense and Mesoporous TiO₂ Films. *Nano. Lett.* **2012**, *12*, 2397–2403.

(47) Gusak, V.; Nkurunziza, E.; Langhammer, C.; Kasemo, B. Real-Time Adsorption and Desorption Kinetics of Dye Z907 on a Flat Mimic of Dye-Sensitized Solar Cell TiO₂ Photoelectrodes. *J. Phys. Chem. C* **2014**, *118*, 17116-17122.

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